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Attestation

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Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

99203194.8

## PRIORITY DOCUMENT

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Der Präsident des Europäischen Patentamts:  
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
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**Blatt 2 der Bescheinigung  
Sheet 2 of the certificate  
Page 2 de l'attestation**

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Demandeur(s):  
GASTEC N.V.

NL-7327 AC Apeldoorn

NETHERLANDS

Stork Engineers & Contractors B.V.

1043 NT Amsterdam

NETHERLANDS  
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Title of the invention:

Titre de l'invention:

Process for the removal of sulphur compounds from gases

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See for original title page 1 of the description



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P49318EP00

Title: Process for the reduction of sulphur dioxide and  
process for the removal of sulphur compounds from gases

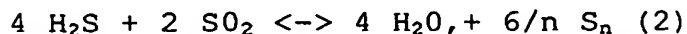
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The invention relates to a process for the catalytic reduction of sulphur dioxide, present in gas mixtures.

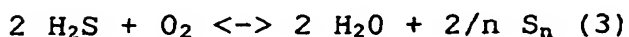
The necessity of purifying gases, which are further treated in chemical processes, or supplied to buyers, or discharged to the atmosphere, from sulphur compounds, in particular hydrogen sulphide, is generally known. Accordingly, there exist a number of processes, which are directed towards the removal of hydrogen sulphide from gas.

The best known and most suitable process for removing sulphur from gas by recovering sulphur from hydrogen sulphide is the so-called Claus process. In this process hydrogen sulphide is converted by oxidation to a considerable extent into elemental sulphur; the sulphur thus obtained is separated from the gas by condensation. The residual gas stream (the so-called Claus tail gas) still contains some  $H_2S$  and  $SO_2$ .

The method of recovering sulphur from sulphur containing gases by the so-called Claus process is based on the following overall reactions:



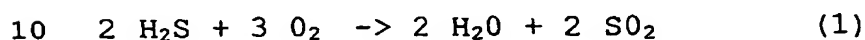
Reactions (1) and (2) result in the main reaction:



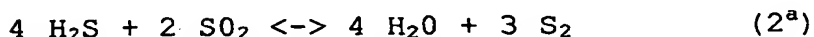
A conventional Claus converter - suitable for processing gases having an  $H_2S$  content of between 50 and 100 % - comprises a burner with a combustion chamber, the so-

called thermal stage, followed by a number of reactors generally two or three - filled with a catalyst. These last stages constitute the so-called catalytic stages.

In the combustion chamber, the incoming gas stream, which is rich in  $H_2S$ , is combusted with an amount of air, at a temperature of approximately  $1200^{\circ}C$ . This amount of air is adjusted so that one third of the  $H_2S$  is fully combusted to form  $SO_2$  in accordance with the following reaction :



After this partial oxidation of  $H_2S$  the non-oxidised part of the  $H_2S$  (i.e. basically two-thirds of the amount offered) and the  $SO_2$  formed react further to a considerable portion, in accordance with the Claus reaction



Thus, in the thermal stage, approximately 60 % of the  $H_2S$  is converted into elemental sulphur.

The gases coming from the combustion chamber are cooled to about  $160^{\circ}C$  in a sulphur condenser, in which the sulphur formed is condensed, which subsequently flows into a sulphur pit through a siphon.

The non-condensed gases, in which the molar ratio of  $H_2S : SO_2$  is unchanged and still 2 : 1, are subsequently heated to about  $250^{\circ}C$ , and passed through a first catalytic reactor in which the equilibrium

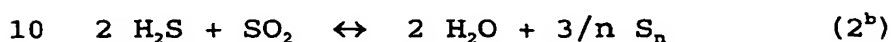


is established.

The gases coming from this catalytic reactor are subsequently cooled again in a sulphur condenser, in which

the liquid sulphur formed is recovered and the remaining gases, after being re-heated, are passed to a second catalytic reactor.

In the Claus process,  $H_2S$  is not quantitatively converted to elemental sulphur, mainly due to the fact that the Claus reaction is an equilibrium reaction and therefore the conversion of  $H_2S$  and  $SO_2$  to elemental sulphur is not complete:



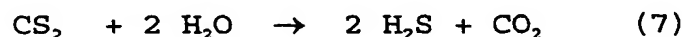
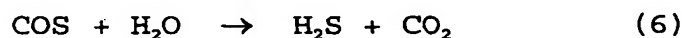
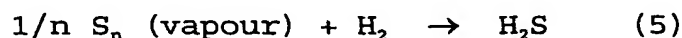
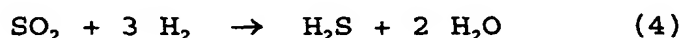
A residual amount of  $H_2S$  and  $SO_2$  remains. Now, generally it is not allowed to discharge residual gas containing  $H_2S$  to the atmosphere, and so the gas is oxidised, with the hydrogen sulphide and other sulphur compounds as well as the elemental sulphur present in the gaseous phase being oxidised to sulphur dioxide. With the environmental requirements becoming stricter, this will not be allowed anymore because the sulphur dioxide emission involved is too high. It is therefore necessary to further treat the residual gas of the Claus installation, the so-called tail gas, in a so-called tail gas treater.

Tail gas processes are known to those skilled in the art. The most well-known tail gas processes are the SCOT process, the BSR Selectox process, the Claus sub-dewpoint processes such as Sulfreen, CBA and MCRC, and the Superclaus<sup>TM</sup> process.

The SCOT process is an effective process for the treatment of tail gas (See GB-A-1, 356,289). In this process the tail gas, together with hydrogen, is passed over a cobalt oxide/molybdenum oxide catalyst on an  $Al_2O_3$  carrier, all sulphur components present thus being catalytically reduced to  $H_2S$ . The total amount of  $H_2S$  is then separated in conventional manner by liquid absorption. One drawback of the SCOT process is that it requires an expensive and complicated installation. Another drawback is the high energy consumption

involved in removing the hydrogen sulphide from the absorbent again.

In the SCOT process a hydrogenation catalyst is used which is based on a carrier material, usually  $\gamma$ - $\text{Al}_2\text{O}_3$ , with a high specific catalytic surface area of typically more than 300  $\text{m}^2/\text{g}$ , the carrier material being provided with active compounds such as molybdenum, cobalt and/or nickel for the hydrogenation function. In the SCOT hydrogenation reactor all sulphur components are converted to  $\text{H}_2\text{S}$  according to



In this process it is essential that all sulphur species are converted to  $\text{H}_2\text{S}$  down to the ppmv level over the hydrogenation catalyst, in order to prevent corrosion and plugging with solid sulphur in downstream equipment. Partial catalytic hydrogenation of  $\text{SO}_2$  to sulphur vapour or a mixture of sulphur vapour and  $\text{H}_2\text{S}$  is not allowed for the SCOT process. To achieve complete hydrogenation therefore high catalyst bed temperatures in the range of 280-330°C, as well as low space velocities are required.

Another possibility of converting hydrogen sulphide in tail gas to elemental sulphur is the so-called BSR Selectox process, described in US-A 4,311,683. According to this process the tail gas is hydrogenated, water is removed and the  $\text{H}_2\text{S}$  containing gas, mixed with oxygen, is passed over a catalyst containing vanadium oxides and vanadium sulphides on a non-alkaline, porous, refractory oxidic carrier.

An important drawback of both the SCOT process and the BSR Selectox process is that in both cases the tail gas,



after hydrogenation of the sulphur components to  $H_2S$ , must first be cooled in order to remove the water for the greater part. Water greatly interferes with the absorption or the oxidation of  $H_2S$ . Due to the high investments involved, the costs of tail gas treatments according to these known methods are high.

In US patent specification No. 4,988,494, it is proposed that the  $H_2S$  concentration in the gas leaving the last catalytic Claus stage is controlled to have a value ranging between 0.8 and 3 % by volume by reducing the quantity of combustion or oxidation air passed to the oxidation stage.

The increase of the  $H_2S$  concentration will result in a decreased  $SO_2$  concentration, however, not to very low levels. For an  $H_2S$  concentration of 0.8 % by volume, the  $SO_2$  concentration will be typically 0.03 - 0.15 % by volume, and this will result in a sulphur recovery efficiency loss of typically 0.09 - 0.45 %.

In the process according to this patent, the  $H_2S$  is selectively oxidised to elemental sulphur in a dry bed oxidation stage.

In EP-A 669,854, published in 1994, a process for sulphur recovery is described which makes use of selective hydrogenation of  $SO_2$  to elemental sulphur. This patent suggests the use of a cobalt-molybdenum catalyst on a  $\gamma$ -alumina support, as is used in the SCOT process.

During the Fourth Sulfur Technology Conference, November 5-6, 1998, Houston, TX, USA, a paper has been presented, "PRO Claus Process: An Evolutionary Enhancement to Claus Performance". In this paper the selective hydrogenation of  $SO_2$  in Claus tail gas to elemental sulphur, followed by selective oxidation of  $H_2S$  to elemental sulphur is described.

In order to perform selective hydrogenation of  $SO_2$  to sulphur vapour, the temperature of the gas should be reduced significantly and the ratio of hydrogen to sulphur dioxide

should be low. The data in the paper show that the reduced temperature needed for a sufficiently selective conversion to sulphur, results in a decrease of overall SO<sub>2</sub> conversion.

The process of selective reduction to elemental sulphur is thus rather restricted in process conditions and requirements, with the consequence, that difficult and costly measures are required to meet the criteria for the selective reduction to elemental sulphur. One example thereof is the necessary reduction of the H<sub>2</sub>-content of the gas mixture. Further disadvantages of the proposed process reside therein, that it does not result in a very low SO<sub>2</sub> and H<sub>2</sub>S content in the final gas, and that the temperature needs to be high, because of the required conversion. On the other hand, high temperatures are not favoured as they promote the reaction of elemental sulphur vapour with hydrogen, resulting in decreased yields.

Accordingly, this process of selective hydrogenation of SO<sub>2</sub> to elemental sulphur is not a viable alternative for providing an increase in sulphur yield.

Even though these considerations direct the skilled person away from using a hydrogenation step in relation to treatment of Claus tail gas, the inventors have realised, that the hydrogenation of sulphur dioxide might provide a new way to improve the sulphur recovery from Claus tail gases. This has become even more important in view of the increasingly strict requirements on sulphur emissions.

In general Claus tail gas comprises in addition to elemental sulphur, H<sub>2</sub>, CO, SO<sub>2</sub> and H<sub>2</sub>S, a considerable amount of water vapour, which amount may be within the range of 10-40% by volume. The water vapour strongly promotes the reversing Claus reaction.



The effectiveness with respect to the removal of  $\text{SO}_2$  by selective conversion to elemental sulphur can in general be adversely affected by the occurrence of reaction 2°.

Here the sulphur once formed reacts back with the water vapour to form hydrogen sulphide and sulphur dioxide.

The substantial removal of water vapour has evident technical disadvantages, such as the necessity of an additional cooling/heating stage, an additional sulphur recovery stage or a hydrogenation stage followed by a water-removing quench stage.

The occurrence of the side reaction mentioned above is partly determined by practical conditions, such as temperature, contact time, water vapour content, sulphur vapour content and catalytic activity, and has the effect that the sulphur yield is decreased.

The present invention has accordingly as one of its objects to provide a process for the removal of sulphur compounds from gas mixtures, in an economic manner, without too much unit operations being necessary. Another object is to improve the sulphur recovery from Claus tail gases, compared to conventional methods. Also it is an object to provide a process for the reduction of sulphur dioxide to hydrogen sulphide and/or elemental sulphur in water containing gas mixtures, which process is suitable for incorporation in various sulphur recovery processes, to improve the sulphur recovery therewith.

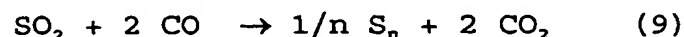
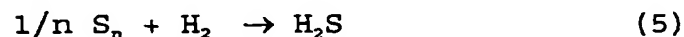
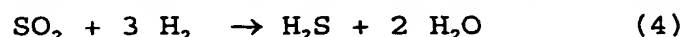
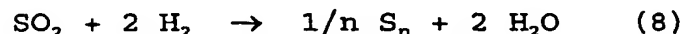
One further object is to prevent that too much sulphur vapour that is already present in Claus tail gas is hydrogenated, resulting in a further load to the subsequent selective oxidation.

The present invention is based on the discovery that the hydrogenation of  $\text{SO}_2$  in Claus tail gas to  $\text{H}_2\text{S}$  and/or to elemental sulphur, can be used as a means for the removal of  $\text{SO}_2$ , in an efficient manner. It has been found that the sulphur recovery can be improved by suppressing the side reactions leading back to the generation of  $\text{SO}_2$  and  $\text{H}_2\text{S}$ . This

can be done in various ways, the most important ones being the use of the reaction kinetics and the use of a catalyst that is not active in promoting the Claus reaction.

The reduction of  $\text{SO}_2$  and sulphur vapour according to

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is thermodynamically complete and is not reversible, in contrast to the Claus reaction.

It has been found that the reduction of  $\text{SO}_2$  (equations 8, 4 and 9) proceeds faster than the reaction of sulphur vapour and hydrogen to  $\text{H}_2\text{S}$ . By applying a sufficiently high space velocity, the majority of the  $\text{SO}_2$  is reduced, without the need to restrict the amount of hydrogen and/or CO in the system or to lower the temperature.

In a first embodiment the invention relates to a process for the catalytic reduction of sulphur dioxide present in a gas mixture at least containing 10 vol.% of water, in which process the gas mixture is passed over a sulphur resistant hydrogenation catalyst in sulphidic form, at a space velocity of at least  $2000 \text{ h}^{-1}$ , in the presence of a reduction component, preferably at least partly consisting of hydrogen, in a molar ratio of reduction component to sulphur dioxide of more than 10 up to 100, at a temperature of  $125^\circ\text{C}$  to  $300^\circ\text{C}$ .

The invention is also concerned with a process for the removal of hydrogen sulphide from gas mixtures, said process comprising the steps of

- converting part of the hydrogen sulphide into sulphur dioxide,
- subjecting the mixture to the Claus reaction in at least one catalytic reactor,

9.

- subjecting the sulphur dioxide present in the resultant gas mixture to a catalytic reduction step using the above described process, and

- selectively oxidising the hydrogen sulphide present  
5 in the resulting gas mixture to elemental sulphur.

The present invention is based on the surprising discovery, that by careful selection of process conditions, it is possible to remove sulphur dioxide from a gas mixture containing substantial amounts of water, without difficulty,  
10 and without the need of difficult measures to obtain the correct process conditions, such as gas composition. The process of the present invention, in view of its careful balance of process conditions, allows the hydrogenation of sulphur dioxide in various gas mixtures, such as Claus tail  
15 gas.

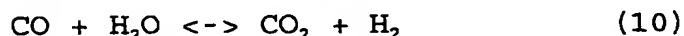
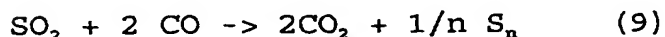
It is to be noted, that the hydrogenation of sulphur dioxide will proceed at least partly to hydrogen sulphide, although also elemental sulphur may be formed. The present inventors have been the first to realise that, when using the  
20 catalytic hydrogenation reaction of  $\text{SO}_2$ , it is important for the sulphur yield that the reverse Claus reaction is suppressed, at least by the selected reaction conditions and preferably also by the properties of the catalyst.

One of the advantages of using the invention resides in  
25 the fact that a high conversion of  $\text{SO}_2$  is obtained at a low temperature, whereas at the same time only a low conversion of sulphur vapour into  $\text{H}_2\text{S}$  is maintained, in the presence of substantial amounts of water vapour.

Important considerations in the process are i.a. the  
30 space velocity, which should be at least  $2000 \text{ h}^{-1}$ , which is very high compared to conventional Claus and Claus tail gas processes. Space velocity is defined as  $\text{Nm}^3 \text{ gas/m}^3$  catalyst/hour. The upper limit can generally be kept below  $12000 \text{ h}^{-1}$ , more preferred below  $10000 \text{ h}^{-1}$ .

35 In the gas containing  $\text{SO}_2$ , also CO is usually present. Because of the reducing properties of CO, this component is

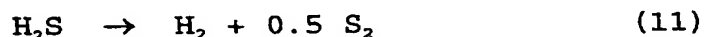
capable of reducing  $\text{SO}_2$ . In this way CO acts in the same way as hydrogen, and a mixture of hydrogen and CO is therefor also suitable for reducing  $\text{SO}_2$ , either directly (Eq. 9) or indirectly via  $\text{H}_2$  production in the water-gas shift reaction (Eq. 10).



In order to obtain a good and fast reduction, the amount of reducing component (hydrogen and/or CO), should be high; on molar basis more than 10 times the amount of sulphur dioxide. The advantage thereof is that there is a fast and efficient removal of  $\text{SO}_2$ .

Excess of hydrogen compared to  $\text{SO}_2$  is normally present in the Claus tail gas of a sulphur recovery unit. The hydrogen in the tail gas is produced in the thermal stage of the sulphur plant, one of the main reactions for hydrogen production being the thermal cracking of  $\text{H}_2\text{S}$

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The excess of hydrogen compared to  $\text{SO}_2$  in the Claus tail gas is determined by the Claus process, and cannot be controlled easily. In case additional hydrogen is required, this can be generated by sub-stoichiometric combustion of fuel gas in the in-line reheaters, or added to the tail gas in the form of a concentrated hydrogen stream from outside battery limits. Removal of hydrogen, as is necessary for the selective reduction of  $\text{SO}_2$  to elemental sulphur as described in EP-A 669,854, is very difficult and cost ineffective. According to the present invention it is not relevant whether sulphur dioxide is converted to hydrogen sulphide or to elemental sulphur.

The process of the invention has the advantage that little or no hydrogenation of sulphur vapour, coming from the

Claus unit occurs, which would otherwise lead to a further load of the subsequent oxidation stage.

The catalyst to be used in the present invention should be catalytically active in the hydrogenation of  $\text{SO}_2$  to elemental sulphur and/or to  $\text{H}_2\text{S}$ . Generally this means that the catalyst preferably consists of a support and a catalytically active material.

As an effective catalytically active material at least one Group VIB, VIIB or VIII, preferably a molybdenum compound is used, or a mixture of molybdenum, nickel and cobalt compounds, optionally in combination with one or more promoting compounds of non-metals.

The active component is present on the carrier in an amount preferably in the range of 0.1-40% by weight, more preferably 0.1-10% by weight calculated on the total weight of the catalyst, and 60-99.9% of a carrier material.

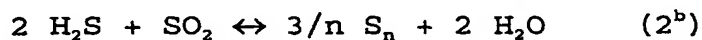
The catalyst has to be in the sulphided form in order to be suitable. Sulphided catalysts are known as such. Generally, sulphiding is done by contacting the catalyst with  $\text{H}_2\text{S}$ , an organic sulphur containing compound, such as dimethyl-disulphide or sulphur, prior to use. The catalyst may contain one or more promoting materials. Suitable promoting materials according to the invention are phosphorus compounds. These can be applied to the catalyst inter alia by impregnation with a soluble phosphorus compound.

It is preferred to use for the reduction step a catalyst on a support, said support having substantially no activity towards the Claus reaction, as defined later on. By this aspect of the invention a further improvement of the sulphur recovery occurs, in view of the absence of the reverse Claus reaction, which reaction would result in the production of  $\text{SO}_2$ . More in particular this embodiment is of importance in the case that the Claus tail gas contains substantial amounts of CO (i.e. over 0.5 % by vol). It has been found that the production of COS, an undesired by-product, leading to a decrease in the sulphur recovery, is

strongly depressed by the use of a hydrogenation catalyst having substantially no catalytic activity towards the Claus reaction.

The properties of the support material depend on the embodiment. In case the Claus activity of the support is not very important, any conventional support for a hydrogenation catalyst may be used. In the preferred embodiment discussed here above, the support consists of a material that is not active towards the Claus reaction. Suitable supports therefor are, i.a. silica,  $\alpha$ -alumina, silica alumina, zirconia, carbon (fibres), carbides, phosphates (such as aluminium phosphate).

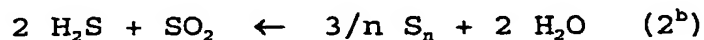
It is noted that in the present invention the absence of Claus activity is defined in the experimental part, preceding the examples. This definition of the Claus activity is based on direct measurement of the Claus reaction activity, according to the reaction



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If a material is Claus active, the presence of water results in the reaction taking place in the direction of  $\text{H}_2\text{S}$  and  $\text{SO}_2$ , with a part of the sulphur being converted to  $\text{H}_2\text{S}$  and  $\text{SO}_2$  again.  $\text{SO}_2$  is then hydrogenated with the  $\text{H}_2$  present to sulphur and water vapour, whereafter the Claus active catalyst converts the sulphur back into  $\text{SO}_2$ . Due to the concurrence of these reactions a catalyst with Claus active sites will in the presence of water give rise to a strong decrease in conversion, according to

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The specific surface area of the catalyst according to the invention can be considerably higher than at least 5



m<sup>2</sup>/g, since a good activity can be obtained with such values. However, it is also possible to use a catalyst having a low BET surface area, such as  $\alpha$ -alumina based hydrogenation catalysts.

5 Preferably, the specific surface area of the catalyst will not be larger than 300 m<sup>2</sup>/g of catalyst. In general no specific additional advantages are gained with higher values.

10 Within the scope of the invention "specific surface area" means the BET surface area as defined by S. Brunauer et al., in J.A.C.S. 60, 309 (1938). The BET surface area is determined by nitrogen adsorption at 77 K according to the so-called three-point measurement. In the calculation the surface area of a nitrogen molecule is set at 16.2 Å<sup>2</sup>.

15 In principle the catalysts can be prepared by the known methods of preparing (supported) catalysts.

According to the process of the invention sulphur dioxide is removed by reduction, by passing a sulphur dioxide containing gas together with a reducing agent containing gas over the sulphided catalyst at an elevated temperature.

20 The reduction is carried out by adding such an amount of reduction component, such as hydrogen or an hydrogen containing gas, to the sulphur dioxide containing gas, using a known per se ratio regulator, that the molar ratio of reduction component to sulphur dioxide is between 10 and 100, and preferably between 10 and 50.

The process according to the invention can be used for the treatment of all gases, which comprise sulphur dioxide.

30 The process according to the invention is eminently suitable for treatment of gas mixtures which do not contain more than 1.0% of SO<sub>2</sub>, because then a normal, adiabatically operating reactor can be used.

In the hydrogenation the inlet temperature of the catalyst bed is selected above 125°C and preferably above 170°C. This temperature is partly dictated by the requirement  
35 that the temperature of the catalyst bed should be above the

solidification temperature of liquid sulphur (115°C) and also above the dew point temperature of the sulphur.

By known per se measures the maximum temperature in the catalyst bed is generally maintained below 300°C and

5 preferably below 250°C.

If the SO<sub>2</sub> content is higher than 1.0% by volume it may be necessary to take steps in order to prevent the temperature in the hydrogenation reactor from becoming too high due to the reaction heat released. Such steps include  
10 for instance the use of a cooled reactor, for instance a tubular reactor, where the catalyst is in a tube which is surrounded by a coolant. Such a reactor is known from European patent specification 91551. A reactor containing a cooling element may also be employed. Further, it is possible  
15 to return the treated gas to the reactor inlet after cooling, and thus an additional dilution of the gas to be hydrogenated is attained.

The process according to the invention can be utilised with particular advantage for the hydrogenation of the  
20 sulphur dioxide containing residual gases coming from a Claus plant. Because of the very high selectivity of the catalyst for the reduction of SO<sub>2</sub>, compared to the reverse Claus reaction, a very important additional advantage is thus obtained in that the removal of water prior to the  
25 hydrogenation is no longer required. If the process according to the invention is used to oxidise the residual gases referred to, these gases are passed directly to a selective oxidation stage.

According to a variant of the process according to the  
30 invention the hydrogenation stage in which the catalyst according to the invention is used is combined with a subsequent hydrogenation stage, wherein elemental sulphur is hydrogenated to H<sub>2</sub>S, followed by absorption of hydrogen sulphide, as described in European patent application 71983.  
35 98% of the sulphur compounds present are thus removed in the part preceding the second hydrogenation, so that the said

second hydrogenation stage and the absorption mass are not unduly loaded. In this way sulphur recovery percentages up to 100% can be achieved.

According to a variant of this process it is possible  
5 after the hydrogenation stage to again employ a selective oxidation according to the invention instead of the absorption mass, a total sulphur recovery percentage between 99.5 and 99.8% being thus attained.

If in the process according to the invention the  
10 sulphur vapour containing gas coming from the hydrogenation stage, optionally after condensation and separation of the greater part of the sulphur, is passed over a bed in which the sulphur is removed by capillary absorption, or the gas is further cooled in a so-called Deep Cooler to below the  
15 solidification temperature of sulphur, see European application 0655414, the sulphur recovery percentage is increased to more than 99.5%.

In a particularly preferred embodiment the catalyst of the invention is used as a separate bed close to the outlet  
20 of the last (second) catalytic Claus reactor. Because of the careful selection of process conditions, the use of such a bed results in a particularly efficient hydrogenation of substantially only the sulphur dioxide to hydrogen sulphide. A further advantage of this embodiment resides therein, that  
25 it is not necessary to install an additional reactor in an existing plant. Instead thereof only a thin layer of catalyst can be placed in the bottom of the said last reactor, using the prevailing reaction conditions in the reactor. Thereby the sulphur dioxide is hydrogenated.

30

#### Experimental part

The Claus activity of a carrier material is established by the following test.

35 A tubular quartz reactor, with an internal diameter of 15 mm, is filled with 4 ml of the carrier material. On the

one hand, the carrier particle size should be less than 10% of the internal reactor diameter and, on the other hand, it should be sufficiently large to avoid excessive pressure drop across the reactor. Such particles may be obtained by

- 5 compressing a carrier powder into tablets, subsequently crushing the tablets and sieving the crushed material with sieves of the appropriate mesh size. Carrier materials in the shape of, for instance, extrusions or beads can simply be crushed and sieved to the appropriate size.

- 10 The filled reactor is placed in a furnace, which ensures an isothermal temperature profile along the axis of the carrier bed. The reactor temperature is measured by an axially placed thermocouple in the bottom, i.e. the outlet side, of the carrier bed.

- 15 The carrier bed is heated to 225 °C in a helium flow, at atmospheric pressure and a GHSV of 6000 Nm<sup>3</sup> gas/ m<sup>3</sup> carrier bed/ hour. At 225 °C, a mixture of 1 vol% H<sub>2</sub>S and 0.5 vol% SO<sub>2</sub> in helium is contacted with the carrier bed, at atmospheric pressure and a GHSV of 6000 Nm<sup>3</sup>/m<sup>3</sup>/h.

- 20 Sulphur vapour produced in the Claus reaction is removed from the product gas by condensation at 120 °C. Subsequently, the sulphur free gas is dried. Methods to remove water vapour from gases are well known to persons skilled in the art. The H<sub>2</sub>S and SO<sub>2</sub> concentrations in the dry product gas are  
25 determined by gas chromatographic analysis.

After a stabilisation period of 24 hours, at 225 °C, the product gas is analysed and the H<sub>2</sub>S and SO<sub>2</sub> conversions are calculated by approximation from the product gas analysis by the following formulas:

H<sub>2</sub>S conversion =

$$\frac{[(\text{vol}\% \text{ H}_2\text{S-reactor-in} - \text{vol}\% \text{ H}_2\text{S-in-dry-product-gas}) / (\text{vol}\% \text{ H}_2\text{S-reactor-in})] * 100\%}{}$$

SO<sub>2</sub> conversion =

5         $\frac{[(\text{vol}\% \text{ SO}_2\text{-reactor-in} - \text{vol}\% \text{ SO}_2\text{-in-dry-product-gas}) / (\text{vol}\% \text{ SO}_2\text{-reactor-in})] * 100\%}{}$

From this the average conversion is calculated:

$$\text{average conversion} = (\text{H}_2\text{S conversion} + \text{SO}_2 \text{ conversion}) / 2$$

A carrier material is considered to have no substantial

10 Claus activity if the average conversion is less than 20%.

Commercially available carrier materials almost invariably exhibit some Claus activity, even if the chemically pure carrier material is theoretically Claus inactive (viz. silica). This is due to traces of precursor materials from which the carrier is produced, or the presence of residual amounts of additives, for instance binders, which have been used to shape the carrier material.

### Examples

20

#### **Example 1**

A commercial  $\gamma\text{-Al}_2\text{O}_3$  catalyst carrier material was tested for Claus activity in an isothermal reactor according to the procedure described in the experimental part.  $\gamma\text{-Al}_2\text{O}_3$  is well known for its Claus activity. The test data are summarised in table 1.

25

Table 1

Feed gas	1 vol% H <sub>2</sub> S, 0.5 vol% SO <sub>2</sub> in He
GHSV	6000 Nm <sup>3</sup> /m <sup>3</sup> /h
Reactor temperature	225 °C
Claus activity = average H <sub>2</sub> S and SO <sub>2</sub> conversion to sulphur	94.5%

### 5 Example 2

A commercial silica carrier material was tested for Claus activity as in example 1. With this material the average H<sub>2</sub>S and SO<sub>2</sub> conversion to sulphur was 12.5%.

10

### Example 3

A Claus process gas containing 1.89 vol% H<sub>2</sub>S, 0.62 vol% SO<sub>2</sub>, 3.85 vol% H<sub>2</sub>, 1.33 vol% CO and 30 vol% H<sub>2</sub>O was contacted with a standard Claus catalyst at 220 °C, atmospheric pressure and a GHSV of 870 Nm<sup>3</sup>/m<sup>3</sup>/h. The product gas was fed to an isothermal reduction reactor, in series with the Claus reactor, containing a sulphided Co/Mo catalyst on a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> carrier as in example 1. The fresh catalyst, in oxidised form (i.e. before sulphidation), contained 4 wt% CoO and 12 wt% MoO<sub>3</sub>, based on the total weight of the catalyst. The B.E.T. surface area was 225 m<sup>2</sup>/g catalyst.

The reactor temperature was set at 225 °C. The product gas composition was determined at three different GHSV's: 3000, 6000 and 9000 Nm<sup>3</sup>/m<sup>3</sup>/h. The results are shown in table 2.

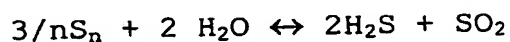
25

With the Co/Mo catalyst on Claus active  $\gamma\text{-Al}_2\text{O}_3$  considerable amounts of COS are formed under the prevailing experimental conditions.

5 **Table 2**

Component	Reduction reactor in	Reduction reactor out		
		GHSV = 3000 Nm <sup>3</sup> /m <sup>3</sup> /h	GHSV = 6000 Nm <sup>3</sup> /m <sup>3</sup> /h	GHSV = 9000 Nm <sup>3</sup> /m <sup>3</sup> /h
H <sub>2</sub> S (vol%)	0.82	1.35	1.00	0.82
SO <sub>2</sub> (vol%)	0.076	0.005	0.010	0.011
COS (vol%)		0.083	0.043	0.042
S-vapour (vol% S <sub>1</sub> )	1.64	1.10	1.48	1.66
H <sub>2</sub> (vol%)	3.85			
CO (vol%)	1.33			
H <sub>2</sub> O (vol%)	31.1			

The SO<sub>2</sub> conversion is the net result of kinetically determined reduction and back formation from sulphur by the reversing Claus reaction:



Under the test conditions, the sulphur vapour in the feed and product gas is a mixture of mainly S<sub>2</sub>, S<sub>6</sub> and S<sub>8</sub>. The average value of n in S<sub>n</sub> at 225 °C is 7.42.

From thermodynamic data it can be calculated that, at a temperature of 225 °C, the natural logarithm of the equilibrium constant for the reversing Claus reaction is:

$$\ln(K_p) = \ln\{[(\text{vol\% } H_2S/100)^2 \times (\text{vol\% } SO_2/100)] / [(\text{vol\% } S_{7.42}/100)^{3/7.42} \times (\text{vol\% } H_2O/100)^2]\} = -11.77$$

From the composition of the product gas leaving the reduction reactor an apparent  $\ln(K_p)$  value can be calculated. For the CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst the apparent  $\ln(K_p)$  values are -13.54, -13.57 and -13.92, at space velocities of 3000, 6000 and 9000 Nm<sup>3</sup>/m<sup>3</sup>/h respectively.

At low space velocity, the apparent  $\ln(K_p)$  approaches the thermodynamic equilibrium value, indicating an increasing influence of the Claus reaction. Although the SO<sub>2</sub> content in the product gas is still low, due to the high reduction activity, the interference with the reversing Claus reaction, suppresses the SO<sub>2</sub> conversion to some extent.

At high space velocities, the apparent  $\ln(K_p)$  deviates more and more from the thermodynamic equilibrium value. In this regime, the SO<sub>2</sub> conversion is determined by the kinetics of the reduction reaction.

#### Example 4

The experiment as in example 3 was repeated with sulphided Mo on the same silica carrier as tested in example 2. The fresh catalyst, in oxidised form, contained 6 wt% MoO<sub>3</sub>, based on the total weight of the catalyst. The B.E.T. surface area was 250 m<sup>2</sup>/g catalyst. As was shown in example 2, the silica carrier exhibits no substantial Claus activity.

The product gas composition was determined at two GHSV's: 6000 and 9000 Nm<sup>3</sup>/m<sup>3</sup>/h. The results are shown in table 3.

Compared to Co/Mo on Claus active  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the catalyst on Claus inactive silica produces far less COS.

The apparent  $\ln(K_p)$  values at 6000 and 9000 Nm<sup>3</sup>/m<sup>3</sup>/h are -14.25 and -13.84 respectively. These figures clearly show that the SO<sub>2</sub> conversion is less influenced by Claus activity than Co/Mo on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, resulting in significantly lower SO<sub>2</sub> emissions from the reduction reactor at medium



space velocity. At the high end of the space velocity range, the kinetics of  $\text{SO}_2$  reduction is the limiting factor. Therefore, the performance of both catalysts is roughly the same at  $9000 \text{ Nm}^3/\text{m}^3/\text{h}$ .

5

Table 3

Component	Reduction reactor in	Reduction reactor out	
		GHSV = 6000 $\text{Nm}^3/\text{m}^3/\text{h}$	GHSV = 9000 $\text{Nm}^3/\text{m}^3/\text{h}$
$\text{H}_2\text{S}$ (vol%)	0.82	1.06	0.82
$\text{SO}_2$ (vol%)	0.076	0.0045	0.012
$\text{COS}$ (vol%)		0.0081	0.0086
S-vapour (vol% $\text{S}_1$ )	1.64	1.46	1.69
$\text{H}_2$ (vol%)	3.85		
$\text{CO}$ (vol%)	1.33		
$\text{H}_2\text{O}$ (vol%)	31.1		

## 10 Example 5

The experiment as in example 3 was repeated with a sulphided commercial Co/Mo catalyst on  $\gamma\text{-Al}_2\text{O}_3$ . The fresh catalyst, in oxidised form, contained 2.5 wt% CoO and 9 wt%  $\text{MoO}_3$ , based on the total weight of the catalyst. The B.E.T. surface area was  $330 \text{ m}^2/\text{g}$  catalyst.

The product gas composition was determined at two GHSV's: 3000 and  $9000 \text{ Nm}^3/\text{m}^3/\text{h}$ . The results are shown in table 4.

Compared to Co/Mo catalyst on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in example 3, the commercial Co/Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, with a different Co and Mo content and surface area, exhibits the same behaviour.

The commercial catalyst also produces considerable amounts of COS. The apparent  $\ln(K_p)$  values are -13.38 and -14.13, at space velocities of 3000 and 9000 Nm<sup>3</sup>/m<sup>3</sup>/h respectively. At low space velocity, the SO<sub>2</sub> conversion is therefore limited by interference with the reversing Claus reaction, as was the case with the Claus active catalyst in example 3

**Table 4**

Component	Reduction reactor in	Reduction reactor out	
		GHSV = 3000 Nm <sup>3</sup> /m <sup>3</sup> /h	GHSV = 9000 Nm <sup>3</sup> /m <sup>3</sup> /h
H <sub>2</sub> S (vol%)	0.82	1.20	0.82
SO <sub>2</sub> (vol%)	0.076	0.0080	0.0090
COS (vol%)		0.0175	0.0255
S-vapour (vol% S <sub>1</sub> )	1.64	1.31	1.68
H <sub>2</sub> (vol%)	3.85		
CO (vol%)	1.33		
H <sub>2</sub> O (vol%)	31.1		

**Example 6**

The experiment as in example 3 was repeated with a sulphided commercial Ni/Mo catalyst on Claus active  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

The composition of the catalyst in oxidised form was specified as NiO: < 25 wt% and MoO<sub>3</sub>: 10-25 wt%, based on the total weight of the catalyst.

The product gas composition was determined at two  
5 GHSV's: 3000 and 9000 Nm<sup>3</sup>/m<sup>3</sup>/h. The results are shown in table 5.

Table 5

Component	Reduction reactor in	Reduction reactor out	
		GHSV = 3000 Nm <sup>3</sup> /m <sup>3</sup> /h	GHSV = 9000 Nm <sup>3</sup> /m <sup>3</sup> /h
H <sub>2</sub> S (vol%)	0.82	1.40	0.85
SO <sub>2</sub> (vol%)	0.076	0.0070	0.0175
COS (vol%)		0.0502	0.0300
S-vapour (vol% S <sub>1</sub> )	1.64	1.08	1.64
H <sub>2</sub> (vol%)	3.85		
CO (vol%)	1.33		
H <sub>2</sub> O (vol%)	31.1		

10

Under the prevailing experimental conditions, Ni/Mo on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> produces considerable amounts of COS. The apparent  
ln(Kp) values for Ni/Mo- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are -13.13 and -13.38, at space  
15 velocities of 3000 and 9000 Nm<sup>3</sup>/m<sup>3</sup>/h respectively, indicating interference with the reversing Claus reaction.

From the experiments in example 3, 5 and 6 it follows that all catalysts on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> exhibit basically the same behaviour, despite differences in metal oxide composition.

With each of these catalysts both the production of COS and the reversing Claus reaction interfere significantly with the reduction of  $\text{SO}_2$  to  $\text{H}_2\text{S}$  and/or sulphur, as opposed to Mo on silica.

- 5 This clearly indicates that Claus activity of the carrier material is a determining factor in the catalyst performance.

#### Example 7

10

The effect of the CO content in the feed gas on COS formation was tested in the following experiment

- 15 A Claus process gas containing 2 vol%  $\text{H}_2\text{S}$ , 1 vol%  $\text{SO}_2$ , 3.85 vol%  $\text{H}_2$ , 30 vol%  $\text{H}_2\text{O}$  and a variable amount of CO was contacted with a standard Claus catalyst at 225 °C, atmospheric pressure and a GHSV of 870  $\text{Nm}^3/\text{m}^3/\text{h}$ . The product gas was fed to an isothermal reduction reactor containing a sulphided Co/Mo catalyst on  $\gamma\text{-Al}_2\text{O}_3$ , identical to the catalyst in example 5. The COS content of the product gas from the reduction reactor was determined at a reactor temperature of 225 °C and a GHSV of 3000  $\text{Nm}^3/\text{m}^3/\text{h}$ . The results are shown in table 6.

Table 6

25

Vol% CO in the feed gas to the reduction reactor	Vol% COS in product gas from the reduction reactor
1.34	0.0313
0.70	0.0082

The experiment shows that the COS production drops very rapidly with decreasing CO content of the feed gas.

It follows from this example that, when maximum SO<sub>2</sub> conversion is not required, catalysts on Claus active carriers perform satisfactory with feed gases having a low CO content. For high SO<sub>2</sub> conversions and feed gases having a high CO content, a catalyst on a Claus inactive carrier is preferred.

10 **Example 8**

A gas containing 0.83 vol% H<sub>2</sub>S, 0.074 vol% SO<sub>2</sub>, 30 vol% H<sub>2</sub>O, 3.85 vol% H<sub>2</sub> and 1.35 vol% CO was contacted, at 225 °C, with sulphided CoMo on γ-Al<sub>2</sub>O<sub>3</sub>, identical to the catalyst in example 5. The feed gas was virtually identical to the feed gas of the reduction reactor in example 5. However, in the experiment of the present example, the feed gas contained no sulphur vapour.

The product gas composition was determined at two GHSV's: 3000 and 6000 Nm<sup>3</sup>/m<sup>3</sup>/h. The results are shown in table 7

Table 7

Component	Reduction reactor in	Reduction reactor out	
		GHSV = 3000 Nm <sup>3</sup> /m <sup>3</sup> /h	GHSV = 6000 Nm <sup>3</sup> /m <sup>3</sup> /h
H <sub>2</sub> S (vol%)	0.83	0.89	0.89
SO <sub>2</sub> (vol%)	0.074	0.00	0.00
COS (vol%)		0.015	0.016
S-vapour (vol% S <sub>1</sub> )	0		
H <sub>2</sub> (vol%)	3.85		
CO (vol%)	1.35		
H <sub>2</sub> O (vol%)	30		

Comparison of table 4 and table 7 shows that

5 hydrogenation of sulphur vapour is a major factor in the production of H<sub>2</sub>S at low space velocities. With sulphur free feed gas, the H<sub>2</sub>S content in the product gas decreases from 1.2 to 0.9 vol%. With no sulphur in the feed, the SO<sub>2</sub> content of the product gas drops below the detection level, due to

10 the reduced conversion of sulphur vapour to H<sub>2</sub>S and SO<sub>2</sub> in the reversing Claus reaction.

From this example it follows that for extremely high SO<sub>2</sub> conversion and minimum loss of sulphur recovery a

15 separate reduction reactor with a preceding sulphur condenser is preferred over an integrated reactor, filled with two stacked layers of respectively a Claus catalyst and a reduction catalyst.

30. 09. 1999

Claims

(59)

1. Process for the catalytic reduction of sulphur dioxide from a gas mixture at least containing 10 vol.% of water, in which process the gas mixture is passed over a sulphur resistant hydrogenation catalyst in sulphidic form,  
5 at a space velocity of at least  $2000 \text{ h}^{-1}$ , in the presence of a reducing component, preferably at least partly consisting of hydrogen, in a molar ratio of reducing component to sulphur dioxide of more than 10 up to 100, at a temperature of  $125^{\circ}\text{C}$  to  $300^{\circ}\text{C}$ .
- 10 2. Process according to claim 1, wherein the catalyst is supported on a carrier material having substantially no activity towards the Claus reaction and having at least one sulphidic hydrogenation component applied to the surface of said carrier material.
- 15 3. Process according to claim 2, wherein the said hydrogenation component is selected from the group of metals of Groups VIB, VIIB and VIII of the periodic table of elements.
- 20 4. Process according to claim 3, wherein the hydrogenation component is based on cobalt and/or molybdenum.
5. Process according to claims 1-4, wherein the gas mixture, after the said reduction, is passed through a dry oxidation bed for the oxidation of sulphur compounds, more in particular hydrogen sulphide, to elemental sulphur.
- 25 6. Process according to claims 2-5, wherein the carrier material is selected from the group of silica,  $\alpha$ -alumina, silica alumina, zirconia, carbon (fibres), carbides, phosphates (such as aluminium phosphate).
- 30 7. Process according to claims 1-6, wherein the said space velocity is less than  $12000 \text{ h}^{-1}$ , preferably less than  $10000 \text{ h}^{-1}$ .

8. Process for the removal of sulphur contaminants from gas mixtures, said process comprising the steps of

- converting part of the hydrogen sulphide into sulphur dioxide,

5 - subjecting the mixture to the Claus reaction in at least one catalytic reactor,

- subjecting the sulphur dioxide present in resultant gas mixture to a removal step using the process of any one of the claims 1-7,

10 - selectively oxidising the hydrogen sulphide present in the resulting gas mixture to elemental sulphur.

9. Process according to claim 8, wherein the said step of selectively oxidising is carried out in a dry oxidation bed.



(59)

Title: Process for the reduction of sulphur dioxide and process for the removal of sulphur compounds from gases

Abstract

The invention is directed to a process for the catalytic reduction of sulphur dioxide from a gas mixture at least containing 10 vol.% of water, in which process the gas mixture is passed over a sulphur resistant hydrogenation catalyst in sulphidic form, at a space velocity of at least  $2000 \text{ h}^{-1}$ , in the presence of a reducing component, preferably at least partly consisting of hydrogen, in a molar ratio of reducing component to sulphur dioxide of more than 10 up to 100, at a temperature of  $125^{\circ}\text{C}$  to  $300^{\circ}\text{C}$ .

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